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The aim of this study was to demonstrate the use of thermogravimetric analysis (TGA) as a potential screening method for monitoring biodiesel production by transesterification of soybean oil with methanol. Soybean oil and commercially available biodiesel were mixed in varying proportions by weight as standards. In addition, mixtures of different biodiesel/soybean oil ratios were also created by periodically interrupting base-catalyzed transesterification of soybean oil with methanol. The mixtures produced by both approaches were analyzed with TGA over a temperature range of 25−500 °C. The results were then compared with analytical data obtained by proton nuclear magnetic resonance spectroscopy (^{1}H NMR spectroscopy), an industry standard for biodiesel quantification. It was found in the TGA experiments that a significant weight loss at ca. 150 °C correlated to the volatilization of biodiesel. The relative weight losses in both sets of mixtures correlated well to the proportion of biodiesel present in the transesterification samples, and the results from both analytical methods were in good agreement (±1.5%). Thus, TGA is a simple, convenient, and economical method for monitoring biodiesel production.

Introduction

Burgeoning demand for biodiesel derived from plant oils has grown significantly over the past decade.[1−9] As is commonly known, the conversion of vegetable oil to biodiesel occurs during a transesterification process in the presence of a catalyst and heat (Figure 1).

Biodiesel production has increased from 500 000 gallons in 1999 to 450 million gallons from Oct. 1, 2006 to Sept. 30, 2007 in the United States alone, and it is expected that this growth will continue to increase at a high rate.[10] It is anticipated that with this growth in production there will be an accompanying need for convenient and rapid analytical means for monitoring biodiesel production. Currently, there are a variety of standard methods for analyzing biodiesel content in mixtures, including gas chromatography (GC),[11] high performance liquid chromatography (HPLC),[12] gel permeation chromatography (GPC),[13,14] proton nuclear magnetic resonance spectroscopy (^{1}H NMR),[7,14] near-infrared (NIR)[15] spectroscopy, and Fourier transform infrared spectroscopy (FTIR).[14] Among these,^{1}H NMR spectroscopy has been used extensively and is often considered a standard characterization method for many chemistries.[7,15,17]

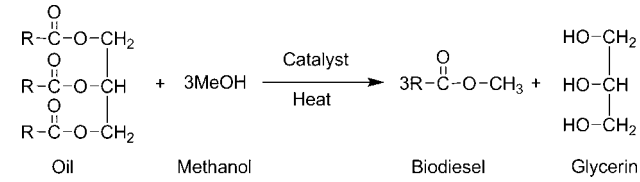

Figure 1. Transesterification reaction of oil with methanol in the presence of sodium hydroxide as catalyst.

Thermogravimetric analysis (TGA) is a technique for characterizing thermal stability of a material (compound or mixture) by measuring changes in its physicochemical properties expressed as weight change as a function of increasing temperature.[18] Therefore, the change in mass of a substance is measured as a function of increasing temperature and the change is correlated to the thermal stability of a material, which is directly related to the material's volatility or thermal degradation to gaseous products. It is proposed that TGA can be used as a fast, low cost, screening method of biodiesel conversion. Thus, the biodiesel industry may be able to use this technique to monitor the yield of biodiesel in order to aid in determining

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(1) *The Biodiesel Handbook*; Knothe, G.; Gerpen, J. V.; Krahl, J. Eds.; American Oil Chemists Society Press: Champaign, IL, 2005.
(2) Ma, F.; Hanna, M. A. *Bioresour. Technol.* **1999**, *70*, 1–15.
(3) Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. *Nature* **2005**, *438*, 178.
(4) Srivastava, A.; Prasad, R. *Renewable Sustainable Energy Rev.* **2000**, *4*, 111–133.
(5) Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakaran, A.; Bruce, D. A.; Goodwin, J. G., Jr. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353–5363.
(6) Freedman, B.; Pryde, E. H.; Mounts, T. L. *J. Am. Oil Chem. Soc.* **1984**, *61*, 1638–1643.
(7) Neto, P. R. C.; Caro, M. S. B.; Mazzuco, L. M.; Nascimento, M. G. *J. Am. Oil Chem. Soc.* **2004**, *81*, 1111–1114.
(8) Wildes, S. *Chem. Health Saf.* **2002**, *9*, 24–26.
(9) Mushrush, G. W.; Beal, E. J.; Hughes, J. M.; Wynne, J. H.; Sakran, J. V.; Hardy, D. R. *Ind. Eng. Chem. Res.* **2000**, *9*, 3945–3948.
(10) Statement of Keith Collins, Chief Economist, U.S. Department of Agriculture before the U.S. Senate Committee on Appropriations Subcommittee on Agriculture, Rural Development, and Related Agencies. Economic Issues Related to Biofuels, August 26, 2006; Agricultural Research Service, Northern Plains Research Lab: Sidney, Montana;www.usda.gov (accessed 9/11/08).
(11) Plank, C.; Lorbeer, E. *J. Chromatogr. A.* **1995**, *697*, 461–468.
(12) Holčapek, M.; Jandera, P.; Fischer, J.; Prokeš, B. *J. Chromatogr. A.* **1999**, *858*, 13–31.
(13) Knothe, G. *Trans ASAE* **2001**, *44*, 193–200.
(14) Dube, M. A.; Zheng, S.; McLean, D. D.; Kates, M. *J. Am. Oil Chem. Soc.* **2004**, *81*, 599–603.
(15) Knothe, G. *J. Am. Oil Chem. Soc.* **2000**, *77*, 489–493.
(16) Knothe, G. *J. Am. Oil Chem. Soc.* **1999**, *76*, 795–800.
(17) Reddy, C. R. V.; Oshel, R.; Verkade, J. G. *Energy Fuels* **2006**, *20*, 1310–1314.
(18) Coats, A. W.; Redfern, J. P. *Analyst* **1963**, *88*, 906–924.

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Table 1. Comparison of TGA with Other Methods Known for the Quantitation of Biodiesel

quantification method	advantages	disadvantages
TGA	No reagent or solvent required	Does not differentiate among different fatty acid methyl esters in biodiesel
	Differentiates easily between biodiesel and plant oil	
	Relatively inexpensive	
^{1}H NMR	Simple, accurate and precise in determining the biodiesel content	Deuterated solvents required ($CDCl_3$ in the present case)
		Instrumentation relatively more expensive
GC	Can differentiate among glycerides, methyl esters and glycerol	Standard solutions are required
		Cumbersome to calculate direct conversion
NIR	No solvent required	Can not quantify low levels of contaminants
	Can differentiate among soybean oil, biodiesel and glycerol	
HPLC	Differentiates among mono-, di- and triglycerides, methyl esters and glycerol	External solvents and standards are required to determine particular components of the mixture
		Cumbersome to calculate direct conversion

the complete conversion time. It is important to note that it is proposed that this technique is used only to monitor transesterification progress and not to determine biodiesel product quality. This can ensure that the conversions discontinued at the proper time will lead to reduced production time, thus increasing the overall efficiency of the biodiesel industry. The TGA technique has been used to characterize biodiesel and oils,[19−21] but these studies did not specifically evaluate the use of TGA as a method for evaluating its efficacy for measuring the extent of oil to biodiesel conversion at any time during the transesterification process, as proposed in the present work.

The TGA instrument consists of a precision mass balance, which records the initial and instantaneous mass of a sample, and a furnace, which increases the temperature in a linear relationship with time (the range of temperatures obtained typically being between 20 and 1000 °C). Mass measurements are performed in air or in an inert gas such as nitrogen or argon. The advantages and limitations of TGA as a method of quantitating biodiesel production in comparison to other methods are tabulated in Table 1.

This paper examines the agreement of TGA and ^{1}H NMR spectroscopy in determining biodiesel content in soybean oil with the aim of evaluating TGA as a viable alternative analytical method for monitoring biodiesel production in research as well as in industrial settings.

Experimental Procedures

Mixtures of laboratory grade biodiesel and soybean oil were prepared and analyzed by TGA and ^{1}H NMR spectroscopy. TGA results were then compared to ^{1}H NMR results in order to determine the accuracy and precision of the TGA analysis of biodiesel. In addition, sample mixtures were analyzed during the conversion of soybean oil to biodiesel catalyzed by sodium hydroxide, a commonly used catalyst in the industry.

Materials

The materials used in this study were commercially refined soybean oil obtained from Watkins E. Inc. Sodium hydroxide, methanol, anhydrous magnesium sulfate ($MgSO_4$), and hexanes were all obtained from Fisher Scientific and were used as received. The biodiesel used as the external standard for TGA was prepared using our previous protocol.[17]

Preparation of Standard Mixtures of Biodiesel and Soybean Oil. Mixtures ofcommercial soybean oil and biodiesel from the aforementioned sources were prepared. In more detail, the biodiesel was prepared at ambient temperature from soybean oil and methanol using nanocrystalline calcium oxide as the catalyst.[17] This biodiesel was found to be ≥99% pure by ^{1}H NMR spectroscopy. The soybean oil was also analyzed by ^{1}H NMR spectroscopy and was also found to be virtually free of contaminants.

The oil and biodiesel were mixed in different proportions by weight. For preparing a 50:50 mixture of biodiesel and soybean oil, 10.00 g of soybean oil was first added to a glass vial using an analytical balance. Biodiesel was then added to bring the total weight of the mixture to 20.00 g. The mixture was then mixed thoroughly for 1 min using a vortex mixer. The remaining standard mixtures were prepared similarly. The weight proportions of soybean oil to biodiesel used for the analyses were: 25.00:75.00, 30.00:70.00, 50.00:50.00, 75.00:25.00, and 80.00:20.00. These samples were then analyzed by TGA and ^{1}H NMR spectroscopy.

Preparation of Biodiesel/Soybean Oil Mixtures during Transesterification. Biodiesel/oil mixtures were also prepared by partially transesterifying soybean oil. Using a syringe, 5.00 mL of methanol was added to 0.20 g of sodium hydroxide to generate a 0.74 M solution of sodium hydroxide. This mixture was continuously stirred magnetically at a temperature of 40 °C for 5 min to form a sodium methoxide/sodium hydroxide equilibrium mixture, which was then added to 20.00 mL of soybean oil via a syringe. It should be noted that for this amount of oil, the theoretical amount of methanol required is approximately 3.00 mL for 100% conversion to biodiesel (i.e., a 1:3 molar ratio). However, an excess of 2.00 mL of methanol was supplied to drive the reaction equilibrium nearer to completion and to accelerate the reaction. The mixture was allowed to react at 60 °C in a shaker water bath with continuous stirring of the reactants via swirling of the flask. The reaction was quenched at a predetermined time by adding water (50.00 mL) and hexanes (50.00 mL) to the reaction mixture. Additional hexanes (200.00 mL) was then added to extract the biodiesel and residual soybean oil, and the mixture was allowed to settle for 10 min in a separatory funnel for separation of the two layers. The top layer containing the biodiesel, soybean oil, and hexanes was then isolated, and anhydrous magnesium sulfate was added to remove trace amounts of water. This mixture was then passed through filter paper to remove the magnesium sulfate, and then the filter paper was washed with hexanes (3 × 20 mL) to obtain residual biodiesel and soybean oil. The filtrate was subjected to rotary evaporation to remove the solvent, and then the remaining sample was analyzed by TGA and ^{1}H NMR spectroscopy for the degree of conversion to biodiesel. It is critical that the all the glycerin (the bottom layer in the

(19) Goodrum, J. W. *Biomass Biofuels* **2002**, *22*, 205–211.
(20) Goodrum, J. W.; Geller, D. P.; Lee, S. A. *Thermochimica Acta* **1998**, *311*, 71–79.
(21) Lima, R. J.; Silva, R. B.; Moura, E. M.; Moura, C. R. *Fuel* **2008**, *87*, 1718–1723.

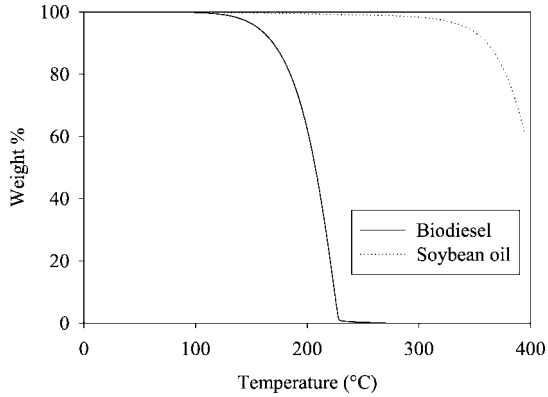

Figure 2. Overlay of thermogravimetric curves for pure biodiesel and soybean oil (wt % versus temperature).

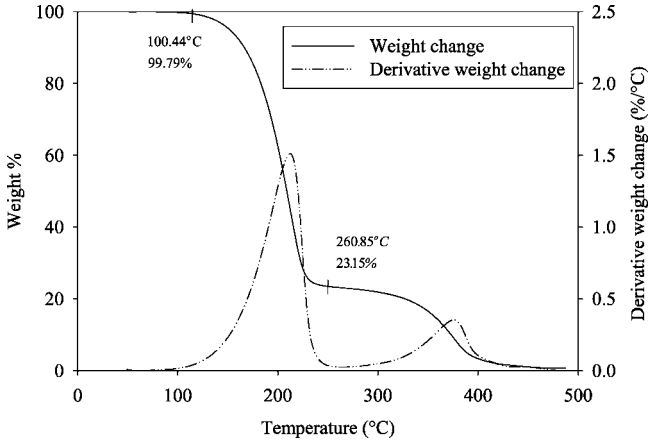

Figure 3. Thermogravimetric curve for a mixture containing 75.00% biodiesel and 25.00% soybean oil.

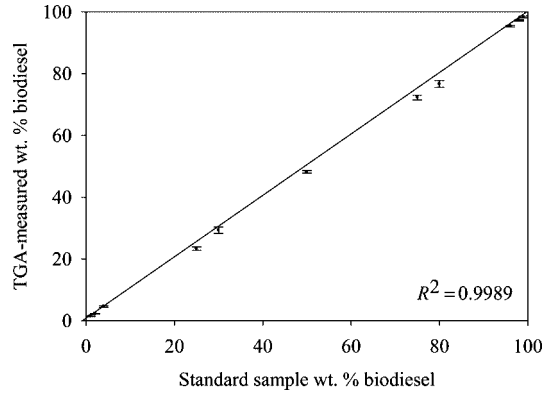

Figure 4. Biodiesel % by weight obtained from TGA analysis plotted against the actual biodiesel weight % in the standard sample.

separatory funnel) is removed from the sample prior to TGA analysis, as this method does not accurately distinguish between biodiesel and glycerin. As detailed in Appendix B, TGA is not an effective method for detecting contaminants such as glycerin, thus it is critical that they are removed by washing prior to characterizing the mixtures.

Analytical Methods. ^{1}H NMR spectra were recorded at ambient temperature on a Varian VXR-400 MHz spectrometer using standard procedures. The chemical shifts were referenced to the residual peaks of $CHCl_3$ in the $CDCl_3$ (7.26 ppm). The relevant signals chosen for integration were those of methoxy groups in the fatty acid methyl esters (3.66 ppm, singlet) and those of the α-methylene protons present in all triglyceride derivatives (2.3 ppm, triplet) of the soybean oil. The conversion was calculated directly from the integrated areas of the aforementioned signals.[18] ^{1}H NMR integrations on five separately prepared standard samples of

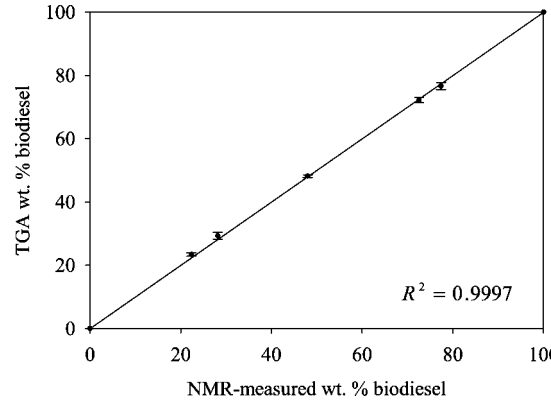

Figure 5. Biodiesel content (wt %) in the standard mixtures obtained by TGA and ^{1}H NMR spectroscopy.

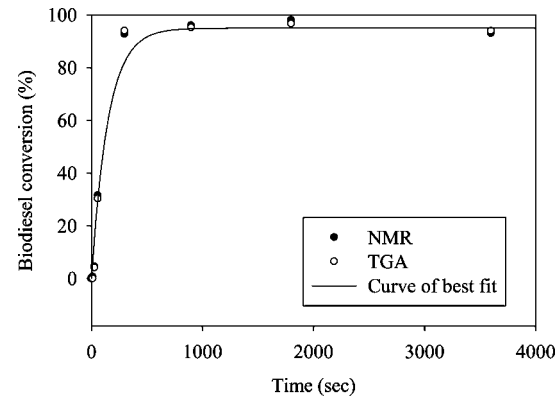

Figure 6. Biodiesel conversion in the transesterification of soybean oil determined by TGA and ^{1}H NMR analysis.

25/75 wt % biodiesel/soybean oil biodiesel mixtures, and on five separately made standard samples of 75/25 wt % biodiesel/soybean oil mixtures indicated that the experimental error was within ± 3% in all cases.

TGA analyses of the biodiesel and oil contents were completed with 10.00 μL samples of biodiesel/oil mixtures heated at a constant heating rate of 10 °C/min in an atmosphere of nitrogen at a constant purge rate of 40 mL/min at the pan. Although other heating rates were examined, 10 °C/min proved to be a reasonable heating rate while minimizing experimental error (see Appendix A). Additional purge rates were not examined because the system used had a fixed purge rate. It was observed that the flow of purge gas promoted pan motion, thus the flow should not substantially exceed the flow rate used. The temperature range employed was 25−500 °C. As further detailed in the following paragraph, the mass loss recorded for biodiesel at ca. 150 °C correlates to the mass percentage of biodiesel present in the sample. Similarly, the mass loss associated with soybean oil (ca. 350 °C) correlates to the mass percentage of soybean oil in the sample. Because these temperatures vary by a relatively large value (ca. 200 °C), this method should be quite effective in distinguishing biodiesel from soybean oil.

Results and Discussion. Figure 2 shows the thermogravimetric plots for pure biodiesel and pure soybean oil. The mass of the biodiesel starts to decrease at approximately after 150 °C, and it continues its decrease until all the biodiesel present in the sample is vaporized. Similarly, evaporation of soybean oil starts at approximately 350 °C. The percentage of biodiesel and soybean oil in a sample could be calculated from the TGA plot of the sample taking into account the first derivative of the weight change of the sample mixture.

As shown in Figure 3, when the mixture is analyzed by TGA, we first used the rate of weight loss ("derivative weight percentage") to determine the relevant temperatures. Here it was assumed that inflection points at the lowest rate of weight change values

correlated to the temperatures of interest. To better indentify the inflection point, however, the second derivative of the mass change was calculated in Excel, and an absolute value greater than 3 wt %/s^2 (approximately 0.02 mg/s^2) was assumed to indicate a significant rate change. Using this approach instead of evaluating the weight loss alone, resulted in a significant increase in the accuracy of the measurement. Our approach resulted in only a maximum of a 5% difference between the measurements and the actual values, whereas the conventional approach resulted in differences as high as 10%. Thus, for example, as seen in Figure 3, the initial inflection point is at 100.44 °C and the second inflection point is at 260.85 °C. Thus, the relative weights were 99.79% and 23.15%, respectively, corresponding to a difference of 76.64% and indicating a biodiesel content, which is in good agreement with the actual value of 75.00%. The initial loss of 0.21% weight of the sample is attributed to the possible presence of volatile impurities.

Typically, and as is consistently assumed in this paper, the amount of biodiesel present in a sample is equal to the mass percentage that lies between the condition where the biodiesel mass drops (at ca. 150 °C) and the condition where all the biodiesel is vaporized and the mass remains constant. The biodiesel/soybean oil TGA plots were compared with plots from known mixtures, thus allowing a determination of the percent by weight of biodiesel in the sample obtained from the transesterification reaction.

The biodiesel yields as measured by TGA analysis of the standard biodiesel/soybean oil mixtures were very similar to their actual values based on weight percent in those mixtures (Figure 4). The linear fit between the two data series results in an R^2 value of 0.9989, which confirms this conclusion. The TGA biodiesel analyses were also plotted as a function of the ^{1}H NMR analyses as seen in Figure 5. The data are typically within ±1.5% of agreement, with the largest difference being ±4.5%.

The linear fit between these two methods showed an R^2 value of 0.9997. Again, the linear regression analysis suggests that TGA accurately quantifies the amount of biodiesel present.

Figure 6 shows biodiesel production as a function of transesterification time as determined by ^{1}H NMR spectroscopy and by TGA. It is important to note in these experiments that there are varying amounts of partially transesterified oil, unlike the previously detailed experiments with the standard mixtures that contained pure biodiesel and pure soybean oil with all the glycerin removed. Thus, the data depicted in Figure 6 are more representative of actual laboratory or industrial production conditions. It is seen that there is good correlation between the two characterization methods. These results suggest that TGA can be efficiently used for analyzing biodiesel contents within ±1.5% (the average of the differences between TGA and NMR measurements) in vegetable oil transesterification reactions.

Conclusions

Our results suggest that thermogravimetric analysis (TGA) is an effective method, which is typically within ±1.5% relative to the proton NMR method for estimating the percentage of biodiesel in transesterification reaction mixtures. This method was validated with the existing proton NMR spectroscopic method for this analysis, and the two methods produced results that were very comparable. With respect to the time required to perform various methods of biodiesel characterization, TGA is comparable to GC and HPLC but requires more time than NMR and NIR. However, the TGA method does not require addition of reagents or solvents to the sample prior to analysis, thus reducing the cost and the probability of errors from such sources.

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Appendices

Appendix A. In all the reported data TGA analyses data, a heating rate of 10 °C/min is used based on experiments where the heating rate was varied and on the experimental error (difference between known value and measured value). In more detail, samples having 50.00 wt % biodiesel were analyzed at heating rates of 10, 25, and 50 °C /min. The results of these analyses are shown in Figure A. It is seen that the relative error (error between actual and measured) obtained in the measurement is generally proportional to heating rate. Therefore, to minimize the error, a heating rate of 10 °C/min was chosen.

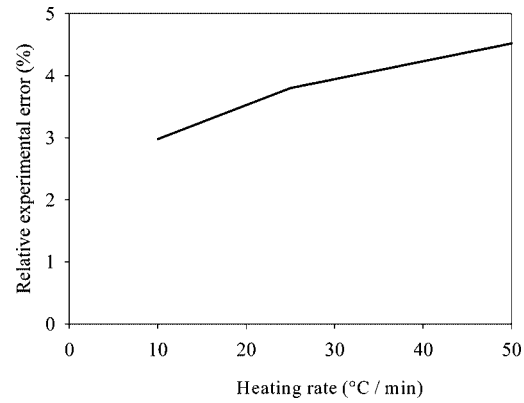

Figure A. Relative Experimental error of TGA measurements as a function of heating rate.

Appendix B. To determine the effect of glycerin on TGA measurements, mixtures were prepared with various levels of residual glycerin. It was found that it was nearly impossible to distinguish between glycerin and biodiesel. For example, a mixture of 33.00% biodiesel, 35.00% glycerin, and 32.00% soybean oil was prepared and characterized using the proposed protocol. This mixture would represent a partially esterified oil that was not properly washed free of glycerin. In the resulting TGA graph in Figure B, it is seen that using the proposed protocol, the graph would suggest that the mixture contains approximately 35% oil and 65% biodiesel. In this case, the TGA results superimpose the amounts of glycerin (~35%) and biodiesel (33%) for a summation of 68% of apparent biodiesel yield. Thus, it is critical that residual glycerins are removed prior to characterization.

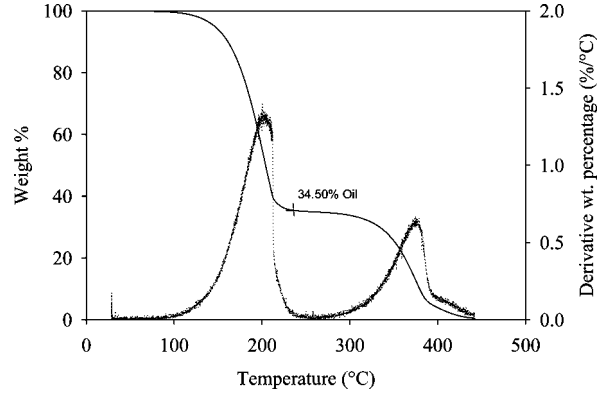

Figure B. Thermogravimetric curve for a mixture containing 33.00% biodiesel, 35.00% glycerin, and 32.00% soybean oil.

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